

APPLICATION

FOR

UNITED STATES LETTERS PATENT

TITLE: THIN FILM MEMBRANE STRUCTURE

APPLICANT: GEORGE M. DOUGHERTY

0994200-11501
T092T"0824660

5

THIN FILM MEMBRANE STRUCTURE**FIELD OF THE INVENTION**

The present invention relates generally to microelectromechanical systems (MEMS), and more particularly to a thin film membrane structure and methods of making such membranes.

BACKGROUND

Developers of microelectromechanical systems (MEMS) often wish to produce device designs that require the fabrication of completely closed hollow structures. These hollow structures are difficult to realize using traditional micromachining processes, because in order to create a hollow cavity by the removal of a sacrificial layer, access holes must be left by which an etchant can reach the sacrificial material. If these holes are not to compromise the structure, they must be placed far apart, making it necessary to etch for a long time to remove the sacrificial material.

For structures such as sealed vacuum cavities and immersible ultrasonic transducers, these etch holes must be sealed by a subsequent material deposition. This requirement precludes the use of standard etch windows, instead requiring the fabrication of very thin slits that can be more readily sealed. This complicates the fabrication process and places restrictions on the device design. The sealing deposition itself can deposit unwanted material inside the hollow spaces, degrading internal structures.

5 It is known that thin layers of polycrystalline silicon
(polysilicon) can sometimes be permeable to hydrogen fluoride
(HF) etching solutions, raising the possibility of simply
removing a sacrificial oxide layer through a layer of
overlying polysilicon. The use of permeable polysilicon etch
10 windows have been useful in creating hollow vacuum cavities.
The HF resistance of thin polysilicon films used for MOSFET
gates has also been investigated. Some studies have been
done to determine the process conditions required to obtain
permeable polysilicon films, and to examine the microstructure
15 of some permeable films.

Unfortunately, MEMS researchers attempting to use
permeable polysilicon have had difficulty obtaining repeatable
results. The recipes used heretofore vary widely, and often
yield impermeable films. A particular recipe may work at
20 certain times and not at others. Further, the physical origin
of the film permeability has remained unclear. If the
processing of permeable polysilicon films were better
understood, the use of such films could greatly simplify
complicated process flows and new device designs might become
25 practical.

SUMMARY

In one aspect, the invention features a membrane
structure comprising a silicon film having a grain structure
including grains defining pores therebetween.

30 In another aspect, the invention is directed to a
membrane structure comprising a silicon film including grains
having gaps formed therebetween to define individual pores.
The maximum cross-sectional dimension of any one grain is
approximately equal to the thickness of the film.

5 Various implementations of the invention may include one or more of the following features. The lateral dimension of any pore is less than that of any grain. The lateral dimension of the pores is between about 10 and 50 nanometers (nm). The thickness of the film is less than or equal to
10 about 150 nm. The thickness of the film is between about 50 and 150 nm. The roughness of the film is approximately equal to its thickness. The film forms a filter. The film is conformal to an underlying surface. A structural layer is provided to support the film. A conformal layer is formed on
15 the film to provide a selected chemical or biological function.

In yet another aspect, the invention is directed to a membrane filter structure comprising a silicon film having a grain structure including grains defining pores therebetween.
20 A lateral dimension of the pores is between about 10 and 50 nm and the maximum diameter of any one grain does not exceed the thickness of the film.

In still another aspect, the invention features a method of fabricating a membrane structure. The method comprises
25 forming a sacrificial layer over a first surface of a substrate and forming a silicon layer over the sacrificial layer. The silicon layer is formed such that it has a grain structure including grains defining pores therebetween wherein the maximum diameter of any one grain does not exceed the
30 thickness of the membrane structure. The sacrificial layer is removed.

Various implementations of the invention may include one or more of the following features. The method may further include forming a passageway through the substrate. A
35 conformal layer may be formed over the silicon layer to provide a selected chemical or biological function.

5 In still another aspect, the invention is directed to a method of fabricating a membrane structure comprising forming a sacrificial layer over a surface of a substrate. A structural layer is formed over the sacrificial layer and a silicon layer is formed over the structural layer. The
10 silicon layer is formed such that it has a grain structure including grains defining pores therebetween wherein the maximum diameter of any one grain does not exceed the thickness of the membrane structure. The sacrificial layer is removed.

15 In yet another aspect, the invention features a method of fabricating a membrane filter structure. The method comprises forming a sacrificial layer over a first surface of a substrate. A silicon film is grown over the sacrificial layer at a temperature near the tensile-to-compressive transition
20 temperature of the film such that the silicon film has a grain structure including grains defining pores therebetween wherein the maximum diameter of any one grain does not exceed the thickness of the membrane filter structure. The sacrificial layer is removed.

25 Various implementations of the invention may include one or more of the following features. The silicon film is formed under a near zero-stress condition. The silicon film has a residual stress within the range of about -50 to 50 mega-Pascals or between about -100 to 100 mega-Pascals. The
30 silicon film is grown such that a lateral dimension of any pore is less than that of any grain. The silicon film is grown such that a lateral dimension of the pores is between about 10 and 50 nm. The silicon film is grown such that the thickness of the film is between about 50 and 150 nm. The
35 silicon film is grown such that a roughness of the film is approximately equal to its thickness. The method may further

5 include forming a conformal layer on the silicon film to provide a selected chemical or biological function. The method may also include monitoring the residual stress of the silicon film.

10 An advantage of the invention is that it provides a single step method for making a thin film filter membrane. The filter membrane contains nanoscale pores that allow gases, liquids and dissolved molecules to pass through the membrane while preventing a larger species from passing. The pores form as a result of the controlled grain structure of the
15 membrane and no additional processing is required to form the pores. Removal of underlying material is easily achieved by immersing in an etching solution, or by other well-known etching techniques, yielding a free-standing membrane structure.

20 The details of one or more embodiments of the invention are set forth in the accompanying drawings and in the description below. Other features, objects and advantages of the invention will be apparent from the description and drawings, and from the claims.

25

DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic, cross-sectional view of a membrane structure in accordance with the present invention.

30 FIGS. 2A-2E are schematic, cross-sectional views of various stages in the fabrication of the structure of FIG. 1.

FIG. 3 is a plot of residual stress versus deposition temperature for various films.

5 FIGS. 4A-4E are scanning electron microscope (SEM) micrographs of various films across the temperature range of 590-610° Centigrade(C).

FIG. 5 is a cross-sectional SEM micrograph of the film shown in FIG. 4C.

10 FIG. 6 is a plan view, low-voltage SEM micrograph of the film shown in FIG. 4C.

FIG. 7 is a plot of X-ray diffraction data for the films shown in FIGS. 4A, 4C and 4E.

FIG. 8 is a plot of reflectometry data for the films shown in FIGS. 4A, 4B, 4C and 4E. (No data is shown for the film of FIG. 4D as no fused quartz wafer was included for that deposition.)

FIGS. 9A-9D are a series of SEM micrographs of the same permeable film exposed to hydrogen fluoride for increasing periods of time.

FIG. 10 is a SEM micrograph of a representative early clearing area as seen in FIGS. 9A-9B.

FIG. 11 is a SEM micrograph of the film of FIG. 4B after a two-hour annealing at 600°C.

25 Like reference symbols and reference numbers in the various drawings indicate like elements.

DETAILED DESCRIPTION

The present invention is directed to a thin film membrane structure and methods of making such membranes. The structure may be used as a filter. The present invention will be described in terms of several representative embodiments and methods. As discussed, the membrane of the present invention may be made of polycrystalline silicon. Alternatively, the membrane may be formed by depositing a silicon film in an

5 initially amorphous state and then annealing the film to develop large silicon grains.

As shown in FIG. 1, a membrane structure 10 may be composed of polycrystalline silicon having a surface roughness approximately equal to a membrane thickness "T". The membrane
10 is made up of silicon grains 12 of a cross-sectional dimension or diameter "D" approximately equal to the membrane thickness "T". The film thickness "T" can be between about 50 and 150 nanometers (nm). The silicon grains are separated by grooves or gaps 14 that form pores 16. The pores lead completely
15 through the membrane, and they are found at the bottom of the gaps. The pores 16 have lateral dimensions "L" that are smaller than those of the silicon grains. A typical pore cross-sectional dimension "L" is on the order of 10-50 nm.

An essential aspect of the filter membrane 10 is that the
20 pores 16 are self-assembled during the formation process of the film. There is no lithographic patterning or etching required to define the pores. No electrochemical process, or any other material removal process, is required. The pores form as a consequence of the control of the film growth
25 process. As a result, the filter membrane 10 is much more simple and economical to produce than previously existing configurations.

As shown in FIGS. 2A-2D, the filter membrane structure 10 may be fabricated by growing a sacrificial support layer 20 on
30 a substrate 22. The sacrificial layer 20 may be a thermally grown layer of silicon dioxide (SiO_2). The substrate 22 may be a 4-inch (100) silicon wafer. Other substrates, of course, could be used, for example a fused quartz wafer. An optional structural layer 24, such as a layer of silicon or silicon
35 nitride, may be deposited above the sacrificial layer 20. The optional structural layer 24 provides additional structural

5 rigidity after the filter membrane is released from the substrate. In this case, a portion of the filter membrane is supported by the optional structural layer 24 (FIG. 2A).

Next, as shown in FIG. 2B, a polysilicon thin film 26 can be deposited over the sacrificial support layer 20 and the optional structural layer 24. By way of example, a film 26 may be deposited using a low pressure chemical vapor deposition (LPCVD) system. The film may be deposited by flowing 125 standard cubic centimeters per meter (sccm) of pure silane (SiH_4) at a pressure of about 550 mTorr. The deposition temperature may be about 600° Celsius (C). The deposition rate and the deposition time may be selected such that the film 26 is no thicker than about 150 nm.

The polysilicon film 26 may also be deposited using a disilane gas source. Additionally, the film may be deposited at various pressures between about 150 mTorr and 1 Torr. Reducing the deposition pressure will lower the growth temperature. The deposition temperature may also range between about 580-610°. Additionally, the flow rate of the deposition gas should be sufficient to maintain the deposition pressure, and prevent buildup of reaction products in the deposition chamber. The flow rate required for this will depend heavily on the size of the deposition hardware being used. Alternatively, various deposition processes other than LPCVD may be used to deposit the film 26. For example, a CVD or a plasma-enhanced CVD process may be used to form the film 26.

Next, as shown by FIG. 2C, the sacrificial support layer 20 may be removed by chemical etching through the pores of the filter membrane layer 26. For example, the support layer 20 may be etched using hydrogen fluoride (HF). Alternatively,

5 other techniques, such as vapor-phase etching and plasma etching, may be used to remove the sacrificial support layer.

After the support layer has been removed, a free-standing thin film membrane 26 is formed as shown in FIG. 2D. The filter membrane 26 has the configuration and structure of the
10 membrane 10 illustrated in FIG. 1. That is, the surface roughness of the filter membrane is approximately equal to the membrane thickness T . The film is made up of silicon grains of a cross-sectional dimension or diameter approximately equal to the membrane thickness. Certain of the silicon grains are
15 separated by deep grooves or gaps. As discussed, pores that lead completely through the membrane structure are found at the bottom of these gaps. The pores have lateral dimensions that are smaller than those of the silicon grains, with typical pore diameters in the 10-50 nm range.

20 Finally, as shown in FIG. 2E, a passageway, channel or opening 28 may be formed through the back side of the substrate 22 for the passage of a fluid, as represented by arrow "A", to be filtered. The passageway 28 may be formed by, for example, etching or laser ablation.

25 A variation of the above-described method would be to deposit a conformal layer (not shown) onto the filter membrane 26. The thickness of the conformal layer would be selected such that the pores are not sealed. The conformal layer can provide increased structural strength. It can also be used to
30 tailor the chemical or biological functionality of the membrane filter structure. For example, the surface characteristic of the membrane structure can be modified to provide a certain biological selectivity to the structure. The conformal layer, for instance, may be a self-assembled
35 mono (SAM) layer for biological applications or parylene for structural rigidity.

5 The simplest method of manufacturing the thin film filter
membrane 10, 26 is to control the deposition parameters of a
single LPCVD process, such that the silicon film is deposited
at a temperature that results in a film that is nearly free of
intrinsic residual stress. At such conditions, the film
10 takes on the required structure. The specific depositions
parameters, as noted, will vary depending on the silicon
source gas and the deposition pressure and temperature chosen.
When the structure 10, 26 is deposited by LPCVD, it is highly
conformal to an underlying surface, which is a valuable
15 quality not available with approaches used in the past.

In a series of experiments, a total of 22 undoped
polysilicon films were deposited at different temperatures
across the temperature range of 590-610°C. The deposition
rates were in the range of 10 nm per minute, at a deposition
20 temperature of ten minutes for all films.

Polysilicon thin films were deposited using a front-
injection, horizontal, hot-wall LPCVD system (Tystar Titan
II). A pure SiH₄ atmosphere was used, at a pressure of 550
mTorr, and the deposition temperature was varied over the
25 range of 590-610°C. The silane flow rate was 125 sccm. The
substrates were 4-inch (100) silicon wafers with 100 nm of
thermally grown SiO₂. In addition, for some runs, fused quartz
wafers were also included as substrates to aid in film
characterization. Because extremely thin films may not have
30 the mechanical strength required for MEMS applications, and
because a reduction in permeability has been observed for
films grown beyond about 150 nm of film thickness, a target
thickness of 100 nm was chosen.

The thickness of the deposited films was measured by
35 spectroscopic interferometry using a Nanospec 3000 optical
film thickness measurement system. The residual stress was

5 determined by wafer curvature measured by laser scanning using a Tencor FLX-2320 instrument.

Permeability was judged by immersing each wafer in 49% HF solution. The combination of the thin polysilicon film atop a thin SiO₂ sacrificial layer gave the as-deposited wafers a
10 bright golden appearance due to optical interference. If the underlying SiO₂ was removed by the HF etchant, the color changed from bright gold to dull gray and could easily be judged by the naked eye. In some cases, the wafers were removed from the etchant when only partially cleared, so that
15 the details of this behavior could be examined by optical microscopy.

Selected films were characterized by X-ray diffraction (XRD) using a Siemens D5000 diffractometer. Surface morphology was examined using a JEOL 6300 scanning electron
20 microscope (SEM), in most cases using a 15 nm layer of sputtered gold to provide improved surface resolution. Spectroscopic reflectometry using the Nanospec 3000, as well as atomic force microscopy (AFM) were also performed on selected films.

25 For practical purposes, HF permeability was defined as substantial visible SiO₂ removal within one minute of immersion in the HF etchant. In general, films were clearly either permeable or impermeable; either there was widespread change in the color of the wafer in under a minute, or there
30 was no color change even after several minutes. No effort was made to investigate long-term permeability of the qualitatively impermeable films, since those films are not likely to be practically useful.

FIG. 3 is a plot of the residual stress versus deposition
35 temperature for all of the films, with an indication of whether each film was permeable. It is clear that all the

5 permeable films are found within a well-defined process window located at the transition between tensile and compressive regimes (horizontal line "B"). In a few cases, impermeable films near the high temperature edge of this window showed small regions of permeability near the places where the wafer
10 contacted the slots of the boat in the LPCVD tube. At these places, the films were thinner than usual.

SEM micrographs of selected films across the temperature range are shown in FIGS. 4A-4E. It is clear that a pronounced morphological change is seen near the zero-stress
15 condition corresponding to the process window for the permeable films. The film deposited at the center of the process window (FIG. 4C) is characterized by large 100-200 nm grains which are nearly hemispherical in shape. The roughness of this film is comparable to the film thickness, and small
20 gaps, 10 or 20 nm in size, appear to exist between many of the grains. The somewhat more compressive film deposited at higher temperature (FIG. 4D) shows a similar structure, but with a much smaller grain size that is significantly less than the film thickness. The slightly more tensile film shown in
25 FIG. 4B shows a distinctive morphology of a few large grains protruding through a smooth surface layer. Of the films shown, those in FIGS. 4B, 4C and 4D were found to be permeable.

FIG. 5 is a cross-sectional SEM micrograph of the film
30 shown in FIG. 4C. It is possible to see open boundaries 14 between adjacent grains 12 that extend all the way to the underlying layer 30, which is the layer of 100 nm SiO₂.

FIG. 6 is a higher magnification, low voltage SEM (LVSEM) micrograph of the same film. Pores 16 leading through the
35 film are clearly visible. The smallest are about 10 nm in size, and the largest are about 50 nm.

5 The films shown in FIGS. 4A, 4C and 4E were used to
obtain the X-ray diffraction data shown in FIG. 7. The
diffraction patterns for all three films are very similar,
showing a {311} and {220} texture. The selected 2-theta range
is shown in order to emphasize the only difference between the
10 three patterns: the integrated intensity of the {220} peak
increases relative to the {311} peak as the deposition
temperature is increased and the films become more
compressive.

 Spectroscopic reflectometry data was obtained using the
15 films deposited on quartz substrates, since the optical
effects of the SiO₂ layer and associated interfaces prevented
the collection of good data from the films deposited on
silicon wafers. Data was taken at wavelengths of 436, 640 and
780nm, and only the data at 436 nm showed any overall pattern.
20 The 436 nm data is shown in FIG. 8. In light of the SEM
results, it is clear that only short wavelengths close to the
100-200 nm grain size are likely to distinguish between the
surface morphologies of these films. The roughest film
displays the lowest reflectivity.

25 Partially HF-cleared permeable films demonstrated a
distinctive pattern when inspected using optical microscopy.
A series of micrographs of the same permeable film exposed to
HF for increasing periods of time is shown in FIGS. 9A-9D.
These figures show the clearing behavior of an underlying 100
30 nm SiO₂ layer during 40 seconds exposure to a 49% HF solution.
The dark color indicates regions where the underlying SiO₂ has
been etched away. The SiO₂ film is removed first at discrete
locations 32 (see FIG. 9A). With increasing time, the number
of these locations increases (FIGS. 9B and 9C), and the
35 cleared areas expand asymmetrically to form a complex network

- 5 34. Ultimately, the remaining SiO_2 is removed and the entire film is cleared (FIG. 9D).

Based on this observation, additional SEM study was performed in order to determine if the initial discrete areas were morphologically different from the rest of the film.

- 10 FIG. 10 shows a representative example of these areas, and nothing different about the morphology is apparent. The whitish glow 36 is a charge effect due to the underlying cavity formed by the removal of the sacrificial layer. No anomaly in the grain structure is seen in this area.

- 15 In order to gain further understanding of the structural evolution of these films, an additional test was performed. A sample of the slightly tensile film of FIG. 4B was annealed under nitrogen at 600°C for 2 hours. The result is shown in FIG. 11. Clearly much of the smooth layer has been transformed
20 into large grains 12.

- The experimental results indicate that the permeability of the films is due to the small gaps that exist between the approximately hemispherical grains unique to films grown near the tensile-to-compressive transition temperature. These gaps
25 form pores continuous to the substrate only when the film thickness is comparable to or less than the diameter of the hemispherical grains. Continuous pores can also be found between pairs of large grains, or between large grains and the surrounding smooth surface, in the slightly tensile films.

- 30 Another important observation is that, at least for films of the thicknesses used in the experiments, the process window for permeability is narrow, only about $5\text{-}10^\circ\text{C}$. It is expected that using thinner films may widen the process window. However, device work done using permeable polysilicon suggests
35 that freestanding permeable polysilicon films are fragile, and that thinner films may lack the mechanical integrity to

5 survive the removal of the sacrificial layer without breakage. The narrowness of the process window seems to be the fundamental source of the repeatability problems.

By examining FIG. 3, it is evident that the residual stress is the best indicator of permeability. Regardless of
10 deposition temperature, any film with a residual stress within the range of about -50 to 50 mega-Pascals (MPa) proved to be permeable. Thinner films are permeable if their residual stress is between about -100 and 100 MPa. Other techniques such as reflectometry may be useful, but the residual stress
15 seems the most reliable indicator, and offers the best correlation with the film morphology.

In addition, the data of FIG. 3 show that even within the temperature range that produced permeable films, impermeable films sometimes resulted. A careful review of the process
20 history reveals that these changes were the result of long-term variation on the order of several weeks, and often were separated by a period of equipment maintenance. Variations in actual tube temperature on the order of a few percent (versus the indicated temperature) can result from moving
25 thermocouples, recalibrating temperature controls, or replacing key hardware. Depending on the temperature profile of the tube, a similar variation might result from placing substrates at different positions within the tube. In this study, the substrate wafers were always placed in similar
30 locations.

Nonetheless, the permeability of the obtained films was quite producible over periods of a few days to a few weeks. It would be advisable, in cases where permeable polysilicon is deposited on a routine basis, to routinely monitor the
35 residual film stress so that the process can be continuously tuned to produce films near the center of the process window.

- 5 The process temperature should also be retuned after any instance of tube maintenance, using film residual stress as a guide.

Possible variations to the method of manufacturing the thin film membrane structure 10, 26 include depositing the film in an initially amorphous state and annealing it to develop large silicon grains, which might also form pores at their boundaries. It is also possible to deposit the silicon film at conditions that are slightly removed from the ideal conditions, for example, the films of FIGS. 4B and 4D. These structures possess the required grain structure and associated pores in some areas but not in others. However, they are still permeable overall. In the case of films that are at the tensile, low-temperature extreme of the process window for permeable films, the structure looks like the one in FIG. 4B. The structure does not look entirely like that diagrammed in FIG. 1, but there are local regions where there are clumps of grains that look like FIG. 1, possessing pores between them.

In summary, microfabricated membrane filter structures and methods of their fabrication have been described. The permeability of the filter structure 10, 26 is the result of small (order of 10-50 nm) pores between large (order of 100-200 nm) hemispherical grains that characterize the microstructure at the ideal process conditions. This microstructure occurs within a narrow (about 5-10°C) process window at the transition between tensile and compressive film stress regimes.

Because the process window is so narrow, optimal recipes can vary based on temperature variation within the tube, gradual change of tube parameters over time, and especially as the result of tube maintenance. Presumably, there will appear

- 5 to be significant variation between different models of CVD equipment as well.

Because the permeable microstructure is associated with very low-stress films, measuring the residual stress of the films provides a convenient and effective way of monitoring
10 and controlling the permeability. Films of approximately 100 nm thickness are permeable if their residual stress is within the range of about 50 to -50 MPa. Residual stress measurements offer the surest way of tuning a particular system to produce permeable films repeatedly.

- 15 Due to the economy and ease of manufacture of the filter membrane, and the fact that it is manufactured as silicon using standard thin film deposition techniques, there are many applications in a wide range of MEMS systems and other precision devices. For instance, the filter membrane may be
20 used for separation of biological fluids, for instance, the separation of plasma from whole blood. It may also be used to filter liquids or gases that contain entrained particles, or to form semipermeable membrane coverings for microsensors or other devices.

- 25 A number of embodiments of the invention have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the invention. Accordingly, other embodiments are within the scope of the following claims.

30

00994280 112604
T092T 024650